

# PATENT ABSTRACTS OF JAPAN

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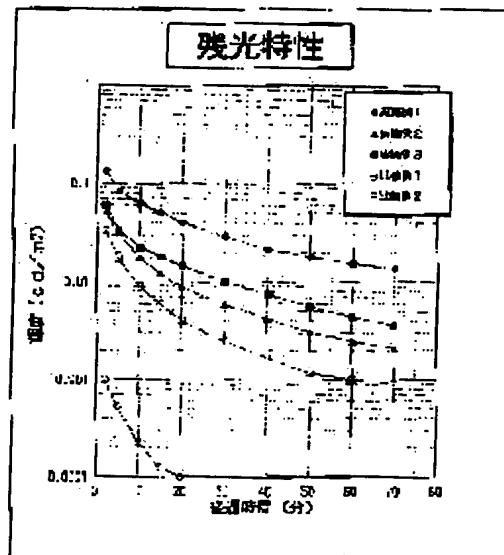
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## (54) PHOTOSTIMULABLE PHOSPHOR

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a photostimulable phosphor having afterglow far longer than that of commercial yellowish-green ZnS:Cu photostimulable phosphors, blue to green luminescence and afterglow, and chemical stability and excellent weather resistance.

**SOLUTION:** This phosphor is represented by the formula:  $m(\text{Sr}_{1-a}\text{M}_{1a})\text{O} \cdot n(\text{Mg}_{1-b}\text{M}_{2b})\text{O} \cdot 2(\text{Si}_{1c}\text{Ge}_c)$   $\text{O}_2:\text{Eu}_x\text{Ln}_y$  (wherein M<sub>1</sub> is Ca or Ba; M<sub>2</sub> is Be, Zn or Cd; Ln is Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr or Mn, and a, b, c, m, n, x and y are in the following ranges:  $0 \leq a \leq 0.8$ ,  $0 \leq b \leq 0.2$ ,  $0 \leq c \leq 0.2$ ,  $1.5 \leq m \leq 2.5$ ,  $0.5 \leq m \leq 1.5$ ,  $1 \times 10^{-5} \leq x \leq 1 \times 10^{-1}$ , and  $1 \times 10^{-5} \leq y \leq 1 \times 10^{-1}$ ) and further contains halogen atoms (F, Cl, Br or I) in an amount in the range of  $1 \times 10^{-5}$  to  $1 \times 10^{-1}$  g.atom/mol of the matrix.



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CLAIMS

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## [Claim(s)]

[Claim 1] It sets to Eu activation silicate phosphorescent materials, and is empirical formula m (Sr<sub>1-a</sub>M<sub>1</sub> a) O-n (Mg<sub>1-b</sub> M<sub>2</sub> b) O-2 (Si<sub>1-c</sub> Gec)O<sub>2</sub>. : Eux Lny It is expressed. Inside M<sub>1</sub> of a formula The element more than a kind chosen from calcium and Ba, and M<sub>2</sub> The element more than a kind chosen from Be, Zn, and Cd, Co-activating agent Ln Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, aluminum, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr And the element more than a kind chosen from Mn is shown, and the inside a, b, c, m, nx, and y of a formula is in the following range. And said fluorescent substances are phosphorescent materials characterized by containing the halogen more than a kind chosen from F, Cl, Br, and I in the range of  $1 \times 10^{-5} - 1 \times 10^{-1}$  g-atm / one mol of parents.

$0 \leq a \leq 0.80 \leq b \leq 0.20 \leq c \leq 0.21.5 \leq M \leq 2.50.5 \leq n \leq 1.51 \times 10^{-5} \leq x \leq 1 \times 10^{-11} \times 10^{-5}$

$\leq y \leq 1 \times 10^{-1}$  -- [Claim 2] Phosphorescent materials according to claim 1 characterized by being an element more than a kind as which said co-activating agent Ln was chosen from Dy, Nd, Tm, Sn, In, and Bi [claim 3] the time of carrying out an excitation afterbaking temperature up at which it is based on the ultraviolet rays and/or the light of the range of 140-450nm -- at least -- beyond a room temperature -- setting -- \*\* -- the phosphorescent materials according to claim 1 or 2 characterized by presenting heat fluorescence

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention can be used as indoor, the outdoors, a display [ in / further / dark places, such as underwater, ], and the light source, is excellent in weatherability, has high-persistence, and relates to the phosphorescent materials of the silicate system of the europium main activation which presents green luminescence from blue by excitation of ultraviolet rays and/or a visible ray.

[0002]

[Description of the Prior Art] Even after it gives a certain excitation and phosphorescent materials make it emit light to a fluorescent substance, and suspending excitation, they are fluorescent substances which maintain luminescence. By the way, as for phosphorescent materials, multiple-colorizing of phosphorescent materials, the formation of long afterglow, and weatherability amelioration are called for with diversification of a display, and advanced features. The class of color of luminescence and afterglow was limited, and the conventional phosphorescent materials had bad weatherability, and its afterglow time amount was short.

[0003] By the way, as blue luminescence phosphorescent materials, the S:Cu (Zn, Cd) fluorescent substance is known as a ZnS:Cu fluorescent substance and red luminescence phosphorescent materials as a S:Bi (calcium, Sr) fluorescent substance and yellowish green luminescence phosphorescent materials.

[0004] However, since the chemical stability of a parent is very bad and brightness and the decay characteristic do not have it, either, the above-mentioned (calcium, Sr) S:Bi fluorescent substance is hardly used by current. [ enough ] Moreover, since Cd which is a toxic substance occupies the one half of a parent and cannot satisfy brightness and the decay characteristic, either, a S:Cu (Zn, Cd) fluorescent substance is hardly used by current. Ultraviolet rays decompose and it is easy to carry out melanism also of ZnS:Cu under existence of moisture, and although the decay characteristic is also dissatisfied, since it is cheap, it is used abundantly for [, such as a dial face, a refuge leading sign, etc. of a clock, ] indoor.

[0005]

[Problem(s) to be Solved by the Invention] This invention cancels the above-mentioned fault, has the long decay characteristic, has green luminescence from blue, is still more chemically stable and tends to offer phosphorescent materials excellent in weatherability.

[0006]

[Means for Solving the Problem] That is, this invention is the green luminescence phosphorescent materials from the blue which consists of the following configuration.

- (1) Set to Eu activation silicate phosphorescent materials, and it is empirical formula  $m(\text{Sr}_1-a\text{M}_1\text{O}_n(\text{Mg}_1-b\text{M}_2\text{O}_2)\text{O}_2)$  : Eux Lny It is expressed. The inside of a formula, and M1 The element more than a kind chosen from calcium and Ba, and M2 The element more than a kind chosen from Be, Zn, and Cd, Co-activating agent Ln Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, aluminum, Ga, In, Ti, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr The element more than a kind chosen from Mn is shown, and the inside a, b, c, m, nx, and y of a formula is in the following range. And and said fluorescent substance Phosphorescent materials

- characterized by containing the halogen more than a kind chosen from F, Cl, Br, and I in the range of  $1 \times 10^{-5} - 1 \times 10^{-1}$  g-atm / one mol of parents.  
 $0 \leq a \leq 0.80 \leq b \leq 0.20 \leq c \leq 0.21$ .  
 $5 \leq m \leq 2.50$ .  
 $5 \leq n \leq 1.51 \times 10^{-5} \leq x \leq 1 \times 10^{-11} \times 10^{-5}$ .  
 $\leq y \leq 1 \times 10^{-1}$  [0007] (2) The above characterized by said co-activating agent Ln being an element more than a kind chosen from Dy, Nd, Tm, Sn, In, and Bi (1) Phosphorescent materials of a publication [0008] (3) The above characterized by presenting thermoluminescence at least beyond a room temperature when [ at which it is based on the ultraviolet rays and/or the light of the range of 140-450nm ] carrying out an excitation afterbaking temperature up (1) Or (2) Phosphorescent materials of a publication [0009]  
[The mode of implementation of invention] this invention person etc. is O(Sr and M1)-(Mg and M2) O-(Si, germanium) O2. When examination was advanced centering on the fluorescent substance parent (it is M1 =calcium, and Sr and Ba and they are M2 =Be, and Zn and Cd) of a system, it found out that the fluorescent substance parent suitable for long afterglow-ization existed in the presentation region of the field shown in drawing 1 with a slash. Namely, empirical formula m(Sr and M1) O-n (Mg and M2) O-2 (Si, germanium)O2 It is expressed and the range of  $0.5 \leq n \leq 1.5$  is suitable for m and n by  $1.5 \leq m \leq 2.5$ .  
[0010] And in this invention, while activating by Eu to the above-mentioned fluorescent substance parent Ln (Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, aluminum, Ga, In, Ti, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, and W -- Cr) And by making it coactivate by the element more than a kind chosen from Mn, and making a halogen (element more than a kind chosen from F, Cl, Br, and I) contain It succeeded in optimization of a luminescence pin center,large (Eu) and a content element, and it had the very long decay characteristic, and it was chemically stable and succeeded in obtaining the phosphorescent materials of green luminescence from the blue excellent in weatherability. Also in the above-mentioned co-activating agent Ln, Dy, Nd, Tm, Sn, In, and especially Bi are excellent.  
[0011] In the empirical formula of this invention, the range of  $0 \leq a \leq 0.8$  and good better \*\*  $0 \leq a \leq 0.4$  is suitable, and if the amount a of permutations of Sr (mol) is permuted exceeding 0.8, its effectiveness of the improvement in the decay characteristic will decrease. moreover, the amount b of permutations of Zn (mol) --  $0 \leq b \leq 0.2$  -- the range of  $0 \leq b \leq 0.1$  is preferably suitable, and if it permutes exceeding 0.2, the effectiveness of the improvement in the decay characteristic will decrease. The amount c (mol) which permutes Si by germanium has little effectiveness of the improvement in the decay characteristic, when the range of  $0 \leq c \leq 0.2$  and good better \*\*  $0 \leq c \leq 0.1$  is suitable and 0.2 is exceeded, and brightness also falls.  
[0012] Moreover, m(Sr and M1) O which is the parent constituent of a fluorescent substance, n (Mg and M2) O and 2 (Si, germanium)O2 The range of  $1.7 \leq m \leq 2.3$  and  $0.7 \leq n \leq 1.3$  is preferably suitable. the value of said m and n which determine a presentation ratio --  $1.5 \leq m \leq 2.5$  and  $0.5 \leq n \leq 1.5$  -- If it separates from this range, since compounds other than the purpose are made or a raw material oxide remains, brightness falls.  
[0013] the loadings x (g-atm) of Eu of an activator --  $1 \times 10^{-5} \leq x \leq 1 \times 10^{-1}$  -- the range of  $1 \times 10^{-4} \leq x \leq 5 \times 10^{-2}$  is preferably suitable, less than by  $1 \times 10$  to five, a luminescence pin center,large decreases and the target brightness is not obtained. Moreover, if  $1 \times 10^{-1}$  is exceeded, while a lifting and brightness will fall concentration quenching, the decay characteristic also falls.  
[0014] The range of  $1 \times 10^{-4} \leq y \leq 5 \times 10^{-2}$  is preferably suitable, and less than by  $1 \times 10$  to five, there is no effectiveness in the decay characteristic, and  $1 \times 10^{-5} \leq y \leq 1 \times 10^{-1}$  and since light will be emitted with a co-activating agent element if  $1 \times 10^{-1}$  is exceeded, the loadings y of the co-activating agent element Ln (g-atm) cannot obtain luminescence of a green field from blue.  
[0015] A part of halogen added to the fluorescent substance of this invention works as a fusing agent to diffusion of crystal growth, a luminescence pin center,large, and the co-activating agent element Ln, and raises brightness and the decay characteristic. the addition z of a halogen (g-atm) -- the value as an analysis value of the back, such as washing processing, --  $1 \times 10^{-5} \leq z \leq 1 \times 10^{-1}$  --  $1 \times 10^{-4} \leq z \leq 1 \times 10^{-2}$  is preferably suitable. If less [ if  $1 \times 10^{-1}$  is exceeded, a fluorescent substance will sinter and the processing to fine particles will become difficult and ] than  $1 \times 10^{-5}$ , un-arranging, such as instant luminescence brightness and an afterglow fall, will arise.

- [0016] And the phosphorescent materials of this invention present thermoluminescence beyond a room temperature, when heating and carrying out the temperature up of this fluorescent substance after excitation by the ultraviolet rays and/or the light of the range of 140~450nm.
- [0017] The phosphorescent materials of this invention are compounded as follows. The parent elements Sr and M1 (M1 = calcium, Ba), Mg, M2 (M2=Be, Zn, Cd), Si, germanium, and Activator Eu and co-activating agent Ln use a fluorescent substance raw material in the form of salts, such as a carbonate which can serve as an oxide easily by the oxide or baking respectively, a nitrate, and a chloride. Moreover, a halogen is used in the form of the halogenated compound of configuration element, the activator element Eu, co-activating agent element Ln). And it extracts so that it may become the presentation range of the above-mentioned empirical formula, and it fully mixes by wet or dry type. In addition, a rare earth raw material comrade may make it mix by coprecipitation.
- [0018] Heat-resistant containers, such as an alumina crucible, are filled up with this mixture, and it is calcined once or more at 800~1400 degrees C in 1 ~ 12 hours in the reducing atmosphere of hydrogen content inert gas, or a carbon reduction ambient atmosphere. In addition, also when performing two or more baking, the last baking process is surely performed in reducing atmosphere. This baking object is ground, weak ore acid washing, rinsing, desiccation, screen analysis, etc. are performed, and the phosphorescent materials of this invention are obtained.
- [0019] Drawing 2 is phosphorescent-materials Sr<sub>1.995</sub> MgSi<sub>2</sub>O<sub>7</sub> compounded in the example 1. : Eu<sub>0.005</sub> Dy<sub>0.025</sub> Cl<sub>0.025</sub> It is the X diffraction Fig. which checked the crystal structure. Even if it permuted a part of Sr, Mg, and Si by other elements in the range given in a claim among this fluorescent substance presentation, the almost same result was shown.
- [0020] Drawing 3 is phosphorescent-materials Sr<sub>1.195</sub> calcium<sub>0.8</sub> MgSi<sub>2</sub>O<sub>7</sub> compounded in the phosphorescent materials (curve a) of an example 1, and the example 2. : Eu<sub>0.005</sub> Dy<sub>0.025</sub> Br<sub>0.025</sub> (curve b). As opposed to phosphorescent-materials Sr<sub>0.995</sub> Ba<sub>1.0</sub> MgSi<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub> Dy<sub>0.025</sub> Br<sub>0.025</sub> (curve c) compounded in the example 3 It was what showed the emission spectrum when exciting by 365nm ultraviolet rays, and each emission peak wavelength was 470nm, 500nm, and 450nm. Even if other elements permuted a part of these fluorescent substance presentations with the claim in the range of a publication, the almost same result was shown.
- [0021] Drawing 4 measures and shows the field of an excitation spectrum using the phosphorescent materials of an example 1. measurement of the field of an excitation spectrum – the spectrum of the output side of a spectrophotometer -- fixing wavelength to 470nm, it is what plotted the reinforcement of 470nm (output light) when changing the excitation wavelength of the light which irradiates a sample, and an axis of ordinate means the wavelength of the excitation light which scans the relative luminescence reinforcement of 470nm, and an axis of abscissa. Even if other elements permuted a part of this fluorescent substance presentation with the claim in the range of a publication, the almost same result was shown.
- [0022] Drawing 5 The phosphorescent materials of an example 1 (emission spectrum peak wavelength of 470nm), The phosphorescent materials of an example 2 (emission spectrum peak wavelength of 500nm), The phosphorescent materials of an example 3 (emission spectrum peak wavelength of 450nm), the phosphorescent materials (Sr<sub>1.995</sub> MgSi<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub> --) of the example 1 of a comparison to the phosphorescent materials (ZnS:Cu, emission spectrum peak wavelength of 516nm) of the emission spectrum peak wavelength of 470nm, and the example 2 of a comparison, it irradiated for 30 minutes by 300 luxs using the daylight fluorescent lamp, and the decay characteristic 2 minutes after an exposure halt was come out of and measured. Like the above-mentioned publication, the measuring method irradiated the daylight fluorescent lamp of 30W at the sample, and measured the brightness of afterglow for the afterglow of the fluorescent substance after turning off a lamp with the luminance meter with a visibility filter.
- [0023] It turns out that the example 1 which is phosphorescent materials with an emission spectrum peak wavelength of 470nm has the very remarkable decay characteristic to the example 1 of a comparison so that clearly from drawing 5 . Moreover, although the phosphorescent materials of examples 2 and 3 also differ, as for the luminescent color, they are

known by having the decay characteristic which was excellent even if contrasted with the ZnS:Cu yellowish green luminescence fluorescent substance of the example 2 of a comparison equivalent to a commercial item.

[0024] Drawing 6 is the graph which measured the thermoluminescence property 1 minute after a daylight-fluorescent-lamp 300 lux 15-second exposure and an exposure halt (glow curve) using the Kasei Optonix, Ltd. make and a TLD reader (KYOKKO TLD-1300 amelioration type) with the programming rate of about 8-10 degrees C/second, and showed the result to the phosphorescent materials of examples 1-3. When the temperature up of the phosphorescent materials of examples 1-3 is carried out with the above-mentioned programming rate in the temperature region beyond a room temperature, it turns out that relative heat fluorescence intensity is increasing, so that clearly from curvilinear a-c of drawing 6 .

[0025] The phosphorescent materials of this invention show high brightness high-persistence extremely as mentioned above, and since it is chemically stable, even if it excels in weatherability, and it compares with the phosphorescent materials of the conventional ZnS system, they enable use for a large application, such as not only indoor but an outdoor type. For example, it can apply to the front face of various goods, or can mix on plastics, rubber, vinyl chloride, synthetic resin, or glass, and can use for a road sign, a check-by-looking display, accessories, leisure goods, a clock, OA equipment, educational equipments, a safety sign, construction material, etc. as a molding object or a fluorescent screen.

[0026]

[Example]

[Example 1]

SrCO<sub>3</sub> 29.5 gMgO 4.0 gSiO<sub>2</sub> 12.0 gEu 2O<sub>3</sub> 0.09gD(ies) 2O<sub>3</sub> 0.47gNH<sub>4</sub> Cl 2.3 The raw material of g above was fully mixed, the alumina crucible was stuffed, and it calcinated at 1150 degrees C for 2 hours using the electric furnace in the reducing atmosphere of 2% of 98% hydrogen of nitrogen. Grinding, rinsing, desiccation, and screen analysis were performed for the obtained baking object, and phosphorescent materials were obtained.

[0027] This fluorescent substance is Sr1.995 MgSi 2O<sub>7</sub>. : The emission spectrum when having the presentation of Eu0.005 and Dy0.025 Cl0.025, and the X diffraction Fig. of drawing 2 being shown, and exciting by 365nm ultraviolet rays was as drawing 3 (curve a), and that emission peak wavelength was what has the blue luminescence phosphorescent of 470nm. Moreover, the excitation spectrum had spread to the visible region like drawing 4 . The decay characteristic showed long afterglow so that it might be shown drawing 5 (curve a). Moreover, the glow curve was as drawing 6 . Furthermore, the emission peak wavelength of a fluorescent substance, the decay characteristic (about the luminescence reinforcement of the 2-minute back of an exposure halt and 60 minutes after, it is a ZnS:Cu yellowish green luminescence light storage fluorescent substance luminescence intensity ratio made 100%), and the peak temperature value of a grotesque-curve were indicated to Table 1 and 2.

[0028] [Example 2]

SrCO<sub>3</sub> 17.6 gCaCO<sub>3</sub> 8.0 gMgO 4.0 gSiO<sub>2</sub> 12.0 gEu 2O<sub>3</sub> 0.09gD(ies) 2O<sub>3</sub> 0.47gNH<sub>4</sub> Br 3.3 The raw material of g above was fully mixed, the alumina crucible was stuffed, and it calcinated at 1200 degrees C in the carbon reduction ambient atmosphere for 2 hours using the electric furnace. Grinding, rinsing, desiccation, and screen analysis were performed for the obtained baking object, and phosphorescent materials were obtained.

[0029] This fluorescent substance is Sr1.195 calcium0.8 MgSi 2O<sub>7</sub>. : Eu0.005 and Dy<SUB>0.025 Br0.025 The emission spectrum when having a presentation and exciting by 365nm ultraviolet rays was as drawing 3 (curve b), and that peak was what has the green luminescence phosphorescent of 500nm. Moreover, the decay characteristic showed long afterglow so that it might be shown drawing 5 (curve b). Moreover, the glow curve was as drawing 6 (curve b). Furthermore, the emission peak wavelength, the decay characteristic (luminescence intensity ratio which made 100% the ZnS:Cu yellowish green luminescence light storage fluorescent substance for the luminescence reinforcement of the 2-minute back of an exposure halt and 60 minutes after), and the glow peak temperature value of a fluorescent substance were indicated to Table 1 and 2.

## [0030] [Example 3]

$\text{SrCO}_3$  14.7 g  $\text{BaCO}_3$  19.7 g  $\text{MgO}$  4.0 g  $\text{SiO}_2$  12.0 g  $\text{Eu}_2\text{O}_3$  0.09 g D(ies) 203 0.47 g  $\text{NH}_3$  4 Br The raw material of the 2.68g above was fully mixed, the alumina crucible was stuffed, and three between was calcinated at 1200 degrees C using the electric furnace in 3% reducing atmosphere of 97% hydrogen of nitrogen. Grinding, rinsing, desiccation, and screen analysis were performed for the obtained baking object, and phosphorescent materials were obtained.

[0031] This fluorescent substance is  $\text{Sr}_{0.995}\text{Ba}_{1.0}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}\text{Br}_{0.025}$  The emission spectrum when having a presentation and exciting by 365nm ultraviolet rays was as drawing 3 (curve c), and that peak was what has the bluish green color luminescence phosphorescent of 500nm. Moreover, the decay characteristic showed long afterglow so that it might be shown drawing 5 (curve c). Moreover, the glow curve was as drawing 6 (curve c). Furthermore, the luminescence peak value of a fluorescent substance, the decay characteristic (luminescence intensity ratio which made  $\text{ZnS:Cu}$  yellowish green phosphorescent materials 100% for the luminescence reinforcement of the 2-minute back of an exposure halt and 60 minutes after), and the peak temperature value of a grotesque-curve were indicated to Table 1 and 2.

[0032] [Examples 4-19] The phosphorescent materials of an example 1 and the examples 4-19 which have the presentation of a publication in Table 1 by the same approach were obtained. The luminescence peak value, the decay characteristic (luminescence intensity ratio which made 100% the  $\text{ZnS:Cu}$  yellowish green luminescence light storage fluorescent substance for the luminescence reinforcement of the 2-minute back of an exposure halt and 60 minutes after), and the glow peak temperature value of a fluorescent substance of examples 4-19 were indicated to Table 1 and 2.

[0033] [Examples 1-2 of a comparison] It is  $\text{Sr}_{1.995}\text{MgSi}_{207}$  of the example 1 of a comparison like an example 1 except having omitted combination of the co-activating agent element Ln and a halogen. :  $\text{Eu}_{0.005}$  Phosphorescent materials were obtained. Moreover, the example 2 of a comparison made the reference sample the  $\text{ZnS:Cu}$  yellowish green luminescence phosphorescent materials (LC-G1) by Kasei Optonix, Ltd. The peak value of the emission peak wavelength of these fluorescent substances, the decay characteristic (luminescence intensity ratio which made 100%  $\text{ZnS:Cu}$  yellowish green luminescence phosphorescent materials for the luminescence reinforcement of the 2-minute back of an exposure halt and 60 minutes after), and a grotesque-curve was indicated to Table 1 and 2.

## [0034]

## [Table 1]

	化 学 組 成 式	発光波長 (nm)	残光特性(%)		グローブル (℃)
			5分後	60分後	
実1	$\text{Sr}_{1.995}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}\text{Cl}_{0.025}$	470	480	1540	90
実2	$\text{Sr}_{1.995}\text{Ba}_{0.005}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}\text{Br}_{0.025}$	500	180	250	70
実3	$\text{Sr}_{0.995}\text{Ba}_{1.0}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}\text{Br}_{0.025}$	450	195	440	100
実4	$\text{Sr}_{1.995}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}$	470	60	180	85
実5	$\text{Sr}_{1.995}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}\text{Cl}_{0.025}$	470	870	2530	95
実6	$\text{Sr}_{1.995}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}\text{Br}_{0.025}$	470	705	1830	95
実7	$\text{Sr}_{1.995}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}\text{F}_{0.025}$	470	195	280	80
実8	$\text{Sr}_{1.995}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}\text{Cl}_{0.025}$	470	450	990	90
実9	$\text{Sr}_{1.995}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Dy}_{0.025}\text{Cl}_{0.025}$	470	330	710	80
実10	$\text{Sr}_{1.995}\text{MgSi}_{207} : \text{Eu}_{0.005}\text{Nd}_{0.025}\text{Br}_{0.025}$	470	75	210	70

## [0035]

## [Table 2]

	化 学 組 成 式	発光波長 (nm)	残光特性(%) 5分後	残光特性(%) 60分後	熱安定性 (°C)
実11	$\text{Sr}_{1.995}\text{MgSi}_2\text{O}_7:\text{Eu}_{0.005}\text{Tm}_{0.025}\text{Br}_{0.025}$	470	70	200	80
実12	$\text{Sr}_{1.995}\text{MgSi}_2\text{O}_7:\text{Eu}_{0.005}\text{In}_{0.025}\text{Br}_{0.025}$	470	45	120	75
実13	$\text{Sr}_{1.995}\text{MgSi}_2\text{O}_7:\text{Eu}_{0.005}\text{Bi}_{0.025}\text{Br}_{0.025}$	470	40	110	70
実14	$\text{Sr}_{1.995}\text{MgSi}_2\text{O}_7:\text{Eu}_{0.005}\text{Sn}_{0.025}\text{Br}_{0.025}$	470	45	110	80
実15	$\text{Sr}_{0.995}\text{Ba}_{1.0}\text{MgSi}_2\text{O}_7:\text{Eu}_{0.005}\text{Dy}_{0.025}\text{Br}_{0.025}$	470	45	230	90
実16	$\text{Sr}_{1.995}\text{Mg}_{0.97}\text{Zn}_{0.03}\text{Si}_2\text{O}_7:\text{Eu}_{0.005}\text{Dy}_{0.025}\text{Cl}_{0.025}$	470	525	1330	80
実17	$\text{Sr}_{1.995}\text{MgSi}_{1.95}\text{Ge}_{0.04}\text{O}_{0.04}:\text{Eu}_{0.005}\text{Dy}_{0.025}\text{Cl}_{0.025}$	470	330	1200	80
実18	$\text{Sr}_{1.995}\text{Mg}_{0.97}\text{Cd}_{0.03}\text{Si}_2\text{O}_7:\text{Eu}_{0.005}\text{Dy}_{0.025}\text{Cl}_{0.025}$	470	420	920	75
実19	$\text{Sr}_{1.995}\text{Mg}_{0.97}\text{Be}_{0.03}\text{Si}_2\text{O}_7:\text{Eu}_{0.005}\text{Dy}_{0.025}\text{Cl}_{0.025}$	470	395	900	80
比1	$\text{Sr}_{1.995}\text{MgSi}_2\text{O}_7:\text{Eu}_{0.005}$	470	3	0	80
比2	ZnS:Cu	516	100	100	120

[0036]

[Effect of the Invention] Even if this invention is chemically stable and it compares it with a commercial ZnS system yellowish green luminescence light storage fluorescent substance by adopting the above-mentioned configuration, by high brightness, it enables offer of the blue-green phosphorescent materials which show far long afterglow for the first time, and contributes to multiple color-ized multi-functionalization of a display greatly.

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[Translation done.]

## • \* NOTICES \*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1] It is the graph which showed the 3 yuan state diagram of the O-(Mg and M2) O-(Si, germanium)2 O system oxide which forms the parent of the phosphorescent materials of this invention (Sr and M1).

[Drawing 2] It is the X diffraction Fig. which checked the crystal structure of the phosphorescent materials compounded in the example 1.

[Drawing 3] It is the graph which showed the emission spectrum when exciting by 365nm ultraviolet rays to the phosphorescent materials compounded in the examples 1-3.

[Drawing 4] It is the graph which showed the excitation spectrum in each luminescence SUPEKUTORUPI-KU of the phosphorescent materials of an example 1.

[Drawing 5] It is the graph which compared the decay characteristic of the blue of examples 1-3 and the example 1 of a comparison – green luminescence phosphorescent materials, and the yellowish green luminescence phosphorescent materials of the example 2 of a comparison.

[Drawing 6] It is the graph which showed the thermoluminescence property (glow curve) of the phosphorescent materials of examples 1-3.

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[Translation done.]

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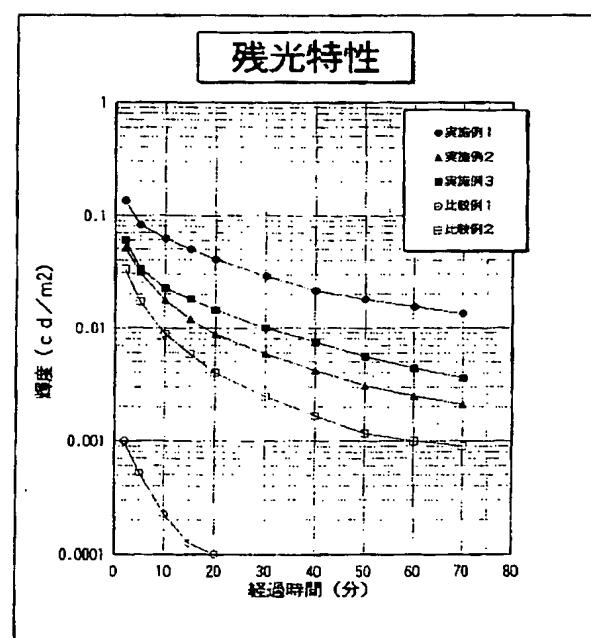
(54)【発明の名称】 褐光性蛍光体

## (57)【要約】

【課題】 市販のZnS : Cu 黄緑色褐光性発光蛍光体に比べても、はるかに長い残光特性を有し、青色から緑色発光及び残光特性を有し、化学的に安定で耐候性に優れた褐光性蛍光体を提供しようとするものである。

【解決手段】  $m(\text{Sr}_{1-a} \text{M}^{\text{I}}_a)_{0.0-n}(\text{Mg}_{1-b} \text{M}^{\text{II}}_b)_{0.0-2}(\text{Si}_{1-c} \text{Ge}_c)_{0.0-\text{Eu}, \text{Ln}_y}$  で表され、式中 $\text{M}^{\text{I}}$ はCa, Ba、 $\text{M}^{\text{II}}$ はBe, Zn, Cd、LnはSc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr, Mnを示し、式中a, b, c, m, n, x, yは下記の範囲にあり、かつ、F, Cl, Br, I等のハロゲン元素を $1 \times 10^{-5} \sim 1 \times 10^{-1}$  g・atm/母体1モルの範囲で含有する褐光性蛍光体である。

$0 \leq a \leq 0.8$ 、 $0 \leq b \leq 0.2$ 、 $0 \leq c \leq 0.2$ 、 $1.5 \leq m \leq 2.5$ 、 $0.5 \leq n \leq 1.5$ 、 $1 \times 10^{-5} \leq x \leq 1 \times 10^{-1}$ 、 $1 \times 10^{-5} \leq y \leq 1 \times 10^{-1}$



## 【特許請求の範囲】

【請求項1】 Eu付活珪酸塩蓄光性蛍光体において、組成式 $m(S_{\text{r}+}M^{1+})O \cdot n(Mg_{\text{r}+}M^{2+})O \cdot 2(S_{\text{i}+}G_{\text{e}})O_2$  : Eu, Ln, で表され、式中 $M^1$  は Ca 及び Ba から選択された一種以上の元素、 $M^2$  は Be, Zn 及び Cd から選択された一種以上の元素、共付活剤 Ln は Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr 及び Mn から選択された一種以上の元素を示し、式中 a, b, c, m, n, x 及び y は下記の範囲にあり、かつ、前記蛍光体は F, Cl, Br 及び I から選択された一種以上のハロゲン元素を、 $1 \times 10^{-5} \sim 1 \times 10^{-1}$  g · atm / 母体 1 モルの範囲で含有することを特徴とする蓄光性蛍光体。

$$0 \leq a \leq 0.8$$

$$0 \leq b \leq 0.2$$

$$0 \leq c \leq 0.2$$

$$1.5 \leq m \leq 2.5$$

$$0.5 \leq n \leq 1.5$$

$$1 \times 10^{-5} \leq x \leq 1 \times 10^{-1}$$

$$1 \times 10^{-5} \leq y \leq 1 \times 10^{-1}$$

【請求項2】 前記共付活剤 Ln が Dy, Nd, Tm, Sn, In 及び Bi から選択された一種以上の元素であることを特徴とする請求項1記載の蓄光性蛍光体

【請求項3】 140 ~ 450 nm の範囲の紫外線及び / 又は可視光による励起後加熱昇温するときに、少なくとも室温以上において熱蛍光を呈することを特徴とする請求項1又は2記載の蓄光性蛍光体

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、屋内や屋外、さらに水中などの暗所における表示や、光源として利用することができ、耐候性に優れ、長残光性を有し、紫外線及び / 又は可視光線の励起によって青色から緑色発光を呈するユーロピウム主付活の珪酸塩系の蓄光性蛍光体に関する。

## 【0002】

【従来の技術】 蓄光性蛍光体は、蛍光体に何らかの励起を与えて発光させた後、励起を停止した後も発光を持続する蛍光体である。ところで、蓄光性蛍光体は、表示の多様化、高機能化に伴い、蓄光性蛍光体の多色化、長残光化及び耐候性改良が求められている。従来の蓄光性蛍光体は、発光・残光の色の種類が限定され、かつ、耐候性が悪く、残光時間が短いものであった。

【0003】 ところで、青色発光蓄光性蛍光体としては、(Ca, Sr)S : Bi 蛍光体、黄緑色発光蓄光性蛍光体としては、ZnS : Cu 蛍光体、また、赤色発光蓄光性蛍光体としては (Zn, Cd)S : Cu 蛍光体が

10

知られている。

【0004】 しかし、上記 (Ca, Sr)S : Bi 蛍光体は、母体の化学安定性が極めて悪く、また、輝度及び残光特性も十分でないため、現在ではほとんど使用されていない。また、(Zn, Cd)S : Cu 蛍光体は、毒性物質である Cd が母体の半分ほど占めており、輝度及び残光特性も満足できないため、現在ではほとんど使用されていない。ZnS : Cu も湿気の存在下で紫外線により分解し、黒化しやすく、残光特性も不満であるが、安価なこともあり、時計の文字盤や避難誘導標識等屋内用に多用されている。

## 【0005】

【発明が解決しようとする課題】 本発明は、上記の欠点を解消し、長残光特性を有し、青色から緑色発光を有し、さらに化学的に安定で耐候性に優れた蓄光性蛍光体を提供しようとするものである。

## 【0006】

【課題を解決するための手段】 即ち、本発明は、下記の構成からなる青色から緑色発光蓄光性蛍光体である。

- 20 (1) Eu付活珪酸塩蓄光性蛍光体において、組成式 $m(S_{\text{r}+}M^{1+})O \cdot n(Mg_{\text{r}+}M^{2+})O \cdot 2(S_{\text{i}+}G_{\text{e}})O_2$  : Eu, Ln, で表され、式中、 $M^1$  は Ca 及び Ba から選択された一種以上の元素、 $M^2$  は Be, Zn 及び Cd から選択された一種以上の元素、共付活剤 Ln は Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr 及び Mn から選択された一種以上の元素を示し、式中 a, b, c, m, n, x 及び y は下記の範囲にあり、かつ、前記蛍光体は、F, Cl, Br 及び I から選択された一種以上のハロゲン元素を $1 \times 10^{-5} \sim 1 \times 10^{-1}$  g · atm / 母体 1 モルの範囲で含有することを特徴とする蓄光性蛍光体。

$$0 \leq a \leq 0.8$$

$$0 \leq b \leq 0.2$$

$$0 \leq c \leq 0.2$$

$$1.5 \leq m \leq 2.5$$

$$0.5 \leq n \leq 1.5$$

$$1 \times 10^{-5} \leq x \leq 1 \times 10^{-1}$$

$$1 \times 10^{-5} \leq y \leq 1 \times 10^{-1}$$

- 40 (2) 前記共付活剤 Ln が、Dy, Nd, Tm, Sn, In 及び Bi から選択された一種以上の元素であることを特徴とする上記(1)記載の蓄光性蛍光体

【0008】 (3) 140 ~ 450 nm の範囲の紫外線及び / 又は可視光による励起後加熱昇温するときに、少なくとも室温以上において熱発光を呈することを特徴とする上記 (1) 又は (2) 記載の蓄光性蛍光体

## 【0009】

【発明の実施の態様】 本発明者等は、(Sr, M<sup>1</sup>)O

50

—(Mg, M<sup>2+</sup>)O—(Si, Ge)O<sub>2</sub>系の蛍光体母体(M<sup>1+</sup>=Ca, Sr, Baで、M<sup>2+</sup>=Be, Zn, Cdである)を中心に検討を進めたところ、図1に斜線で示す領域の組成域に、長残光化に適した蛍光体母体が存在することを見出した。即ち、組成式m(Sr, M<sup>1+</sup>)O·n(Mg, M<sup>2+</sup>)O·2(Si, Ge)O<sub>2</sub>で表され、m, nが、1.5≤m≤2.5で、0.5≤n≤1.5の範囲が適している。

【0010】そして、本発明では、上記の蛍光体母体に対してEuで付活すると共に、Ln(Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr及びMnから選択された一種以上の元素)で共付活させ、かつ、ハロゲン元素(F, Cl, Br及びIから選択された一種以上の元素)を含有させることにより、発光センター(Eu)や含有元素の最適化に成功し、極めて長い残光特性を有し、化学的に安定で耐候性に優れた青色から緑色発光の蓄光性蛍光体を得ることに成功した。上記の共付活剤Lnの中でも、Dy, Nd, Tm, Sn, In及びBiが特に優れている。

【0011】本発明の組成式において、Srの置換量a(モル)は0≤a≤0.8、好ましくは0≤a≤0.4の範囲が適しており、0.8を越えて置換すると残光特性向上の効果が少なくなる。また、Znの置換量b(モル)は0≤b≤0.2、好ましくは0≤b≤0.1の範囲が適しており、0.2を超えて置換すると残光特性向上の効果が少なくなる。SiをGeに置換する量c(モル)は0≤c≤0.2、好ましくは0≤c≤0.1の範囲が適しており、0.2を越えると残光特性向上の効果が少なく、輝度も低下する。

【0012】また、蛍光体の母体構成成分であるm(Sr, M<sup>1+</sup>)O, n(Mg, M<sup>2+</sup>)O及び2(Si, Ge)O<sub>2</sub>の組成比を決める前記m, nの値は1.5≤m≤2.5及び0.5≤n≤1.5、好ましくは1.7≤m≤2.3及び0.7≤n≤1.3の範囲が適しており、この範囲を外れると、目的以外の化合物ができたり、原料酸化物が残存するため、輝度が低下する。

【0013】付活剤のEuの配合量x(g·atm)は、1×10<sup>-5</sup>≤x≤1×10<sup>-1</sup>、好ましくは1×10<sup>-1</sup>≤x≤5×10<sup>-2</sup>の範囲が適しており、1×10<sup>-5</sup>未満では発光センターが少なくなり、目的の輝度が得られない。また、1×10<sup>-1</sup>を越えると濃度消光を起こし、輝度が低下すると共に残光特性も低下する。

【0014】共付活剤元素Lnの配合量y(g·atm)は、1×10<sup>-5</sup>≤y≤1×10<sup>-1</sup>、好ましくは1×10<sup>-1</sup>≤y≤5×10<sup>-2</sup>の範囲が適しており、1×10<sup>-5</sup>未満では残光特性に効果が無く、1×10<sup>-1</sup>を越えると共付活剤元素により発光するため、青色から緑色の領

域の発光を得ることができない。

【0015】本発明の蛍光体に添加するハロゲン元素は、一部融剤として結晶成長と発光センター及び共付活剤元素Lnの拡散に働き、輝度及び残光特性を向上させる。ハロゲン元素の添加量z(g·atm)は、洗浄処理等後の分析値としての値で1×10<sup>-5</sup>≤z≤1×10<sup>-1</sup>、好ましくは1×10<sup>-4</sup>≤z≤1×10<sup>-2</sup>が適している。1×10<sup>-1</sup>を越えると、蛍光体が焼結して粉体への処理が困難となり、1×10<sup>-5</sup>を下回ると、瞬時発光輝度及び残光低下等の不都合が生ずる。

【0016】そして、本発明の蓄光性蛍光体は、140~450nmの範囲の紫外線及び/又は可視光による励起後に、該蛍光体を加熱し昇温するときに、室温以上において熱発光を呈する。

【0017】本発明の蓄光性蛍光体は、次のようにして合成される。蛍光体原料は、母体元素Sr, M<sup>1+</sup>(M<sup>1+</sup>=Ca, Ba), Mg, M<sup>2+</sup>(M<sup>2+</sup>=Be, Zn, Cd), Si, Geと、付活剤Eu及び共付活剤Lnは各々酸化物もしくは焼成により容易に酸化物となりうる炭酸塩、硝酸塩、塩化物などの塩の形で用いる。また、ハロゲン元素はアンモニウム塩、アルカリ金属塩又は上記構成元素(母体構成元素、付活剤元素Eu、共付活剤元素Ln)のハロゲン化合物の形で用いる。そして、上記組成式の組成範囲になるように採取し、湿式又は乾式で充分に混合する。なお、希土類原料同志は共沈で混合させてよい。

【0018】この混合物をアルミナルツボ等の耐熱容器に充填し、水素含有中性ガスの還元雰囲気中又は炭素還元雰囲気中で800~1400°Cで1~12時間で1回以上焼成する。なお、複数焼成を行うときにも、最終焼成工程は必ず還元雰囲気中で行う。この焼成物を粉碎し、弱鉱酸洗、水洗、乾燥、篩分等を行い、本発明の蓄光性蛍光体を得る。

【0019】図2は、実施例1で合成された蓄光性蛍光体Sr<sub>1.995</sub>Mg<sub>0.005</sub>Si<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub>Dy<sub>0.025</sub>C<sub>1.025</sub>の結晶構造を確認したX線回折図である。この蛍光体組成のうち、Sr, Mg, Siの一部を請求項に記載の範囲で他の元素に置換してもほぼ同様の結果を示した。

【0020】図3は、実施例1の蓄光性蛍光体(曲線a)、実施例2で合成された蓄光性蛍光体Sr<sub>1.195</sub>C<sub>a 0.8</sub>Mg<sub>0.005</sub>Si<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub>Dy<sub>0.025</sub>Br<sub>0.025</sub>(曲線b)、実施例3で合成された蓄光性蛍光体Sr<sub>0.995</sub>Ba<sub>1.0</sub>Mg<sub>0.005</sub>Si<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub>Dy<sub>0.025</sub>Br<sub>0.025</sub>(曲線c)に対し、365nm紫外線で励起したときの発光スペクトルを示したもので、それぞれの発光ピーク波長が470nm、500nm、450nmであった。これらの蛍光体組成の一部を請求項に記載の範囲で他の元素で置換してもほぼ同様の結果を示した。

【0021】図4は、実施例1の蓄光性蛍光体を用いて、励起スペクトルの領域を測定して示したものである。励起スペクトルの領域の測定は、分光光度計の出力側の分光波長を470nmに固定し、試料に照射する光の励起波長を変化させた時の470nm（出力光）の強度をプロットしたもので、縦軸は470nmの相対発光強度、横軸はスキャンする励起光の波長を意味する。この蛍光体組成の一部を請求項に記載の範囲で他の元素で置換してもほぼ同様の結果を示した。

【0022】図5は、実施例1の蓄光性蛍光体（発光スペクトルピーク波長470nm）、実施例2の蓄光性蛍光体（発光スペクトルピーク波長500nm）、実施例3の蓄光性蛍光体（発光スペクトルピーク波長450nm）、比較例1の蓄光性蛍光体（Sr<sub>1.995</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub>、発光スペクトルピーク波長470nm）及び、比較例2の蓄光性蛍光体（ZnS:Cu、発光スペクトルピーク波長516nm）に対し、昼光色蛍光ランプを用いて300ルックスで30分間照射し、照射停止2分後の残光特性を測定した。測定方法は、上記の記載のように、30Wの昼光色蛍光ランプを試料に照射し、ランプを切った後の蛍光体の残光を視感度フィルター付き輝度計で残光の輝度を測定した。

【0023】図5から明らかなように、発光スペクトルピーク波長470nmの蓄光性蛍光体である実施例1は、比較例1に対して極めて顕著な残光特性を有することが分かる。また、実施例2、3の蓄光性蛍光体も、発光色は異なるが、市販品に相当する比較例2のZnS:Cu黄緑色発光蛍光体と対比しても優れた残光特性を有していることが分かる。

【0024】図6は、実施例1～3の蓄光性蛍光体に対し、昼光色蛍光ランプ300ルックス15秒照射、照射停止1分後の熱発光特性（グローカーブ）を化成オプトニクス社製、TLDリーダー(KYOKKO TLD-1300改良タイプ)を用いて約8～10°C/秒の昇温速度で測定し、その結果を示したグラフである。図6の曲線a～cから明らかなように、実施例1～3の蓄光性蛍光体は、室温以上の温度域で上記の昇温速度で昇温すると、相対熱蛍光強度が増加していることが分かる。

【0025】本発明の蓄光性蛍光体は、上記のように極めて高輝度長残光性を示し、耐候性に優れかつ化学的に安定なため、従来のZnS系の蓄光性蛍光体に比べても、屋内のみならず屋外用など広い用途への利用を可能にする。例えば、種々の物品の表面に塗布したり、プラスチック、ゴム、塩化ビニール、合成樹脂又はガラス等に混合し、成型体もしくは蛍光膜として、道路標識、視認表示、装飾品、レジャー用品、時計、OA機器、教育機器、安全標識及び建築材等に利用することができる。

#### 【0026】

#### 【実施例】

【実施例1】

SrCO <sub>3</sub>	29.5 g
MgO	4.0 g
SiO <sub>2</sub>	12.0 g
Eu <sub>2</sub> O <sub>3</sub>	0.09 g
Dy <sub>2</sub> O <sub>3</sub>	0.47 g
NH <sub>4</sub> Cl	2.3 g

上記の原料を充分に混合し、アルミナルツボに詰めて電気炉を用い、窒素98%水素2%の還元雰囲気中で1150℃で2時間焼成した。得られた焼成物を粉碎、水洗、乾燥、篩分を行って蓄光性蛍光体を得た。

【0027】この蛍光体は、Sr<sub>1.995</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub>, Dy<sub>0.025</sub>Cl<sub>0.025</sub>の組成を有し、図2のX線回折図を示し、365nm紫外線で励起したときの発光スペクトルは図3(曲線a)のとおりで、その発光ピーク波長は470nmの青色発光蓄光性を有するものであった。また、励起スペクトルは、図4のように可視域まで広がっていた。残光特性は、図5(曲線a)示すように長残光を示した。また、グローカーブは図6のとおりであった。さらに、蛍光体の発光ピーク波長、残光特性(照射停止2分後と60分後の発光強度を、ZnS:Cu黄緑色発光蓄光体を100%にした発光強度比)及びグローカーブのピーク温度値を表1、及び表2に記載した。

【0028】【実施例2】

SrCO <sub>3</sub>	17.6 g
CaCO <sub>3</sub>	8.0 g
MgO	4.0 g
SiO <sub>2</sub>	12.0 g
Eu <sub>2</sub> O <sub>3</sub>	0.09 g
Dy <sub>2</sub> O <sub>3</sub>	0.47 g
NH <sub>4</sub> Br	3.3 g

上記の原料を充分に混合し、アルミナルツボに詰めて電気炉を用い、炭素還元雰囲気中で1200℃で2時間焼成した。得られた焼成物を粉碎、水洗、乾燥、篩分を行って蓄光性蛍光体を得た。

【0029】この蛍光体は、Sr<sub>1.995</sub>Ca<sub>0.8</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub>, Dy<sub>0.025</sub>Br<sub>0.025</sub>の組成を有し、365nm紫外線で励起したときの発光スペクトルは図3(曲線b)のとおりで、そのピークは500nmの緑色発光蓄光性を有するものであった。また、残光特性は、図5(曲線b)示すように長残光を示した。また、グローカーブは図6(曲線b)のとおりであった。さらに、蛍光体の発光ピーク波長、残光特性(照射停止2分後と60分後の発光強度を、ZnS:Cu黄緑色発光蓄光体を100%にした発光強度比)及びグローピーク温度値を表1、及び表2に記載した。

【0030】【実施例3】

SrCO <sub>3</sub>	14.7 g
BaCO <sub>3</sub>	19.7 g

MgO	4.0 g
SiO <sub>2</sub>	12.0 g
Eu <sub>2</sub> O <sub>3</sub>	0.09 g
Dy <sub>2</sub> O <sub>3</sub>	0.47 g
NH <sub>4</sub> Br	2.68 g

上記の原料を充分に混合し、アルミナルツボに詰めて電気炉を用い、窒素97%水素3%還元雰囲気中で120°Cで3間焼成した。得られた焼成物を粉碎、水洗、乾燥、篩分を行って蓄光性蛍光体を得た。

【0031】この蛍光体は、Sr<sub>0.995</sub> Ba<sub>1.0</sub> MgSi<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub> Dy<sub>0.025</sub> Br<sub>0.025</sub> の組成を有し、365 nm紫外線で励起したときの発光スペクトルは図3(曲線c)のとおりで、そのピークは500 nmの青緑色発光蓄光性を有するものであった。また、残光特性は、図5(曲線c)示すように長残光を示した。また、グローカーブは図6(曲線c)のとおりであった。さらに、蛍光体の発光ピーク値、残光特性(照射停止2分後と60分後の発光強度を、ZnS:Cu黄緑色蓄光性蛍光体を100%とした発光強度比)及びグローカーブのピーク温度値を表1及び、表2に記載した。  
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\* 【0032】【実施例4~19】実施例1と同様の方法で表1に記載の組成を有する実施例4~19の蓄光性蛍光体を得た。実施例4~19の蛍光体の発光ピーク値、残光特性(照射停止2分後と60分後の発光強度を、ZnS:Cu黄緑色発光蓄光性蛍光体を100%とした発光強度比)及びグローピーク温度値を表1、及び表2に記載した。

【0033】【比較例1~2】共付活剤元素Ln及びハロゲン元素の配合を省略した以外は、実施例1と同様にして比較例1のSr<sub>1.995</sub> MgSi<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub> 蓄光性蛍光体を得た。また、比較例2は化成オプトニクス社製のZnS:Cu黄緑色発光蓄光性蛍光体(LC-G1)を参照試料とした。これらの蛍光体の発光ピーク波長、残光特性(照射停止2分後と60分後の発光強度をZnS:Cu黄緑色発光蓄光性蛍光体を100%とした発光強度比)及びグローカーブのピーク値を表1、及び表2に記載した。

#### 【0034】

#### 【表1】

	化 学 組 成 式	発光ピーク (nm)	残光特性(%)		グローピーク (°C)
			5分後	60分後	
実1	Sr <sub>1.995</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Dy <sub>0.025</sub> Cl <sub>0.025</sub>	470	480	1540	90
実2	Sr <sub>1.995</sub> Ca <sub>0.1</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Dy <sub>0.025</sub> Br <sub>0.025</sub>	500	180	250	70
実3	Sr <sub>1.995</sub> Ba <sub>1.0</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Dy <sub>0.025</sub> Br <sub>0.025</sub>	450	195	440	100
実4	Sr <sub>1.995</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Dy <sub>0.025</sub>	470	60	180	85
実5	Sr <sub>1.995</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Dy <sub>0.025</sub> Cl <sub>0.025</sub>	470	870	2530	95
実6	Sr <sub>1.995</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Dy <sub>0.025</sub> Br <sub>0.025</sub>	470	705	1830	95
実7	Sr <sub>1.995</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Dy <sub>0.025</sub> F <sub>0.025</sub>	470	195	280	80
実8	Sr <sub>1.995</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Dy <sub>0.025</sub> Cl <sub>0.025</sub>	470	450	990	90
実9	Sr <sub>1.995</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Dy <sub>0.025</sub> Cl <sub>0.025</sub>	470	330	710	80
実10	Sr <sub>1.995</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sub>0.005</sub> Nd <sub>0.025</sub> Br <sub>0.025</sub>	470	75	210	70

【0035】

【表2】

	化 学 組 成 式	発光ピーク (nm)	残光特性(%)		70-8-7 (°C)
			5分後	60分後	
実11	$\text{Sr}_{1-x-y}\text{MgSi}_2\text{O}_7:\text{Eu}_{x-y}, \text{Th}_{0.025}\text{Br}_{0.025}$	470	70	200	80
実12	$\text{Sr}_{1-x-y}\text{MgSi}_2\text{O}_7:\text{Eu}_{x-y}, \text{In}_{0.025}\text{Br}_{0.025}$	470	45	120	75
実13	$\text{Sr}_{1-x-y}\text{MgSi}_2\text{O}_7:\text{Eu}_{x-y}, \text{Bi}_{0.025}\text{Br}_{0.025}$	470	40	110	70
実14	$\text{Sr}_{1-x-y}\text{MgSi}_2\text{O}_7:\text{Eu}_{x-y}, \text{Sn}_{0.025}\text{Br}_{0.025}$	470	45	110	80
実15	$\text{Sr}_{0.995}\text{Ba}_{0.005}\text{MgSi}_2\text{O}_7:\text{Eu}_{0.005}\text{Dy}_{0.025}\text{Br}_{0.025}$	470	45	230	90
実16	$\text{Sr}_{1-x-y}\text{Mg}_{0.9}\text{Zn}_{0.1}\text{Si}_2\text{O}_7:\text{Eu}_{x-y}, \text{Dy}_{0.025}\text{Cl}_{0.025}$	470	525	1330	80
実17	$\text{Sr}_{1-x-y}\text{MgSi}_{1-x-y}\text{Ge}_{x-y}\text{O}_7:\text{Eu}_{x-y}, \text{Dy}_{0.025}\text{Cl}_{0.025}$	470	330	1200	80
実18	$\text{Sr}_{1-x-y}\text{Mg}_{0.9}\text{Cd}_{0.1}\text{Si}_2\text{O}_7:\text{Eu}_{x-y}, \text{Dy}_{0.025}\text{Cl}_{0.025}$	470	420	920	75
実19	$\text{Sr}_{1-x-y}\text{Mg}_{0.97}\text{Be}_{0.03}\text{Si}_2\text{O}_7:\text{Eu}_{x-y}, \text{Dy}_{0.025}\text{Cl}_{0.025}$	470	395	900	80
比1	$\text{Sr}_{1-x-y}\text{MgSi}_2\text{O}_7:\text{Eu}_{x-y}$	470	3	0	80
比2	ZnS:Cu	516	100	100	120

## 【0036】

【発明の効果】本発明は、上記の構成を採用することにより、化学的に安定で、市販のZnS系黄緑色発光蓄光蛍光体と比較しても、高輝度ではるかに長い残光を示す、青色～緑色蓄光性蛍光体を初めて提供可能とし、表示の多色化多機能化に大きく寄与するものである。

## 【図面の簡単な説明】

【図1】本発明の蓄光性蛍光体の母体をなす(Sr, M')O-(Mg, M<sup>2+</sup>)O-(Si, Ge)O系酸化物の三元状態図を示したグラフである。

【図2】実施例1で合成した蓄光性蛍光体の結晶構造を\*

\*確認したX線回折図である。

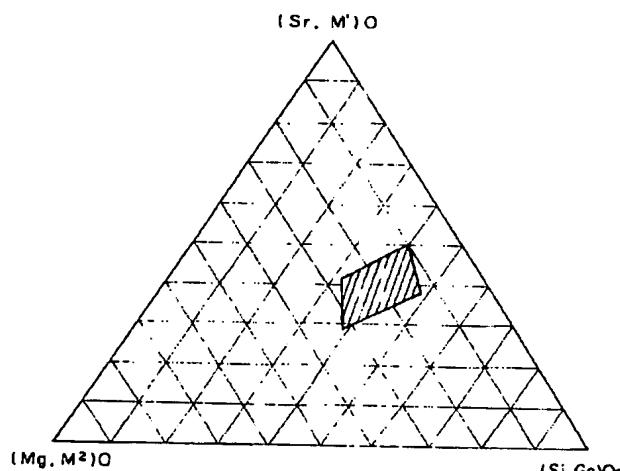
【図3】実施例1～3で合成された蓄光性蛍光体に対し、365 nm紫外線で励起したときの発光スペクトルを示したグラフである。

【図4】実施例1の蓄光性蛍光体の各発光スペクトルピークにおける励起スペクトルを示したグラフである。

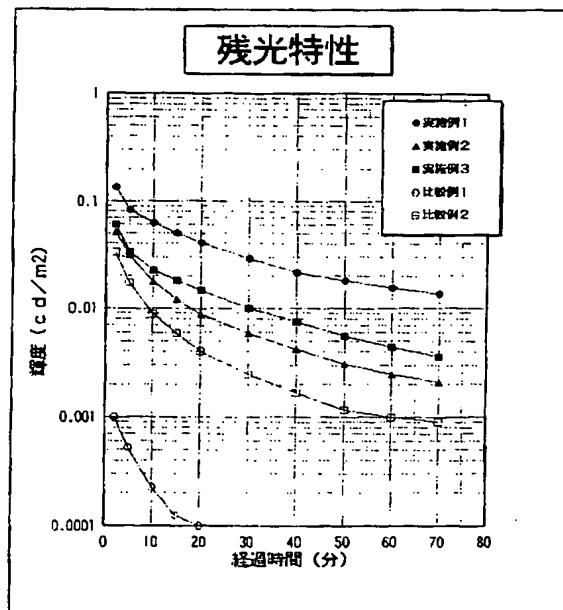
【図5】実施例1～3、及び、比較例1の青色～緑色発光蓄光性蛍光体と、比較例2の黄緑色発光蓄光性蛍光体の残光特性を比較したグラフである。

【図6】実施例1～3の蓄光性蛍光体の熱発光特性(グローカーブ)を示したグラフである。

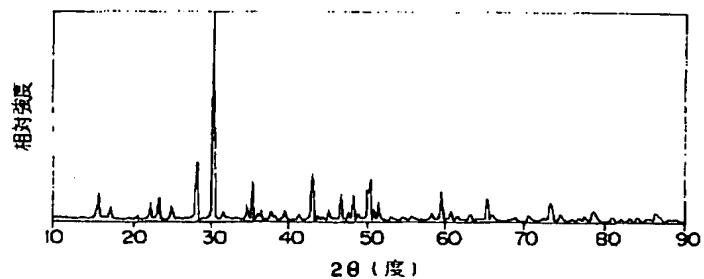
【図1】



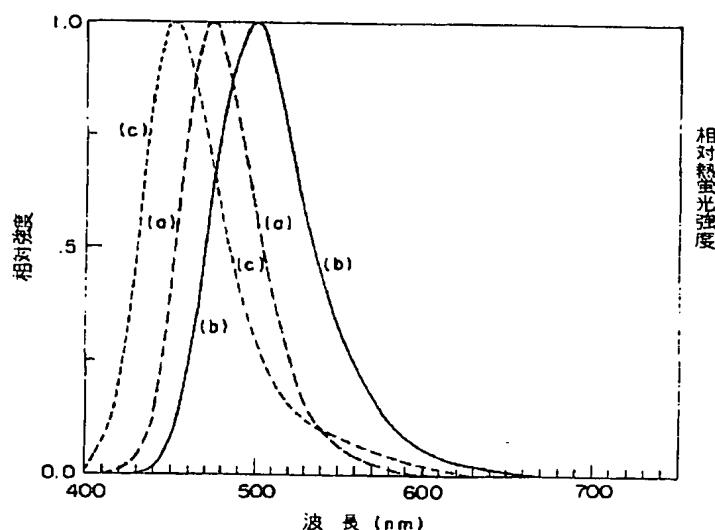
【図5】



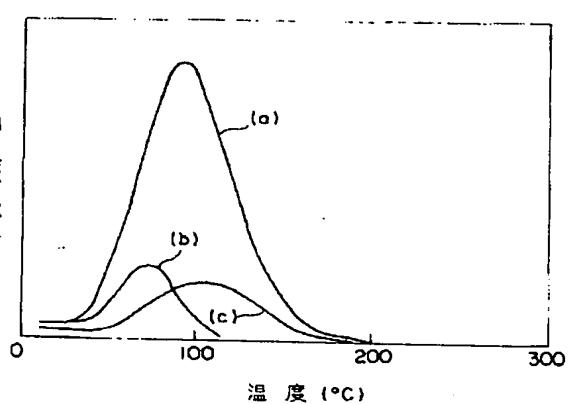
【図2】



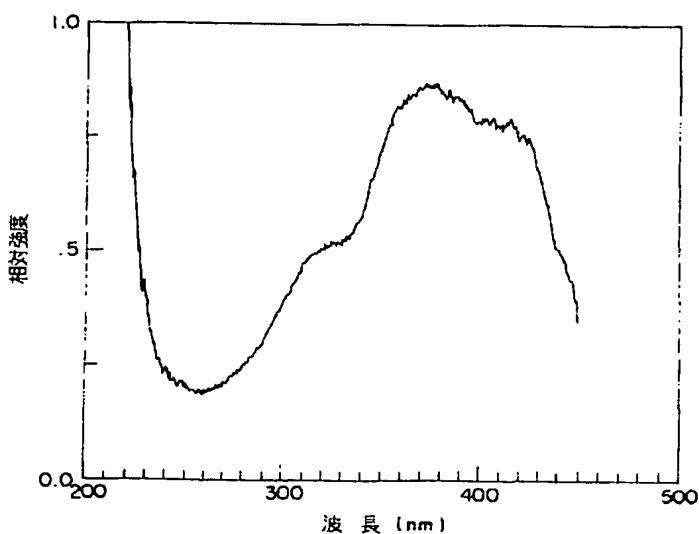
【図3】



【図6】



【図4】



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